

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
4 October 2001 (04.10.2001)

PCT

(10) International Publication Number  
**WO 01/73881 A1**

(51) International Patent Classification<sup>7</sup>: **H01M 8/10**,  
8/08, 8/22

(71) Applicant (for all designated States except US): **SCIEN-  
TIFIC GENERICS LIMITED** [GB/GB]; Harston Mill,  
Harston, Cambridgeshire CB2 5NH (GB).

(21) International Application Number: PCT/GB01/01339

(22) International Filing Date: 26 March 2001 (26.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(72) Inventors; and  
(75) Inventors/Applicants (for US only): **PRIESTNALL,  
Michael, Alexander** [GB/GB]; Scientific Generics Lim-  
ited, Harston Mill, Harston, Cambridgeshire CB2 5NH  
(GB). **EVANS, Michael, Joseph** [GB/GB]; Scientific  
Generics Limited, Harston Mill, Harston, Cambridgeshire  
CB2 5NH (GB). **SHAFFER, Milo, Sebastian, Peter**  
[GB/GB]; 55 Bateman Street, Cambridge CB2 1LR (GB).

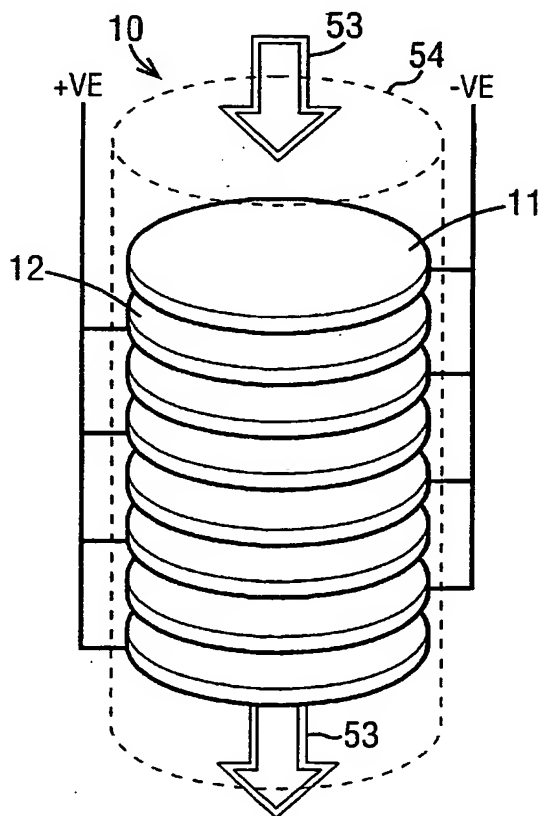
(30) Priority Data:  
0007306.4 24 March 2000 (24.03.2000) GB  
0019622.0 9 August 2000 (09.08.2000) GB  
0019623.8 9 August 2000 (09.08.2000) GB  
0025030.8 12 October 2000 (12.10.2000) GB  
0026935.7 3 November 2000 (03.11.2000) GB  
0027587.5 10 November 2000 (10.11.2000) GB

(74) Agents: **BERESFORD, Keith, Denis, Lewis et al.**; Beres-  
ford & Co., 2-5 Warwick Court, High Holborn, London  
WC1R 5DH (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

[Continued on next page]

(54) Title: MIXED REACTANT FUEL CELLS WITH FLOW THROUGH POROUS ELECTRODES



(57) Abstract: A fuel cell or battery for providing useful electrical power by electrochemical means, comprises: at least one cell; at least one anode and at least one cathode within said cell, and ion-conducting electrolyte means for transporting ions between the electrodes; and is characterised in that: said electrodes are porous and in that means are provided for causing hydrodynamic flow of a mixture of at least fuel and oxidant through the body of said electrodes.

WO 01/73881 A1



CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

MIXED REACTANT FUEL CELLS WITH FLOW THROUGH POROUS  
ELECTRODES

The present invention relates to electrochemical systems and, in particular, to fuel cells or batteries using mixed reactants, that is to say reactants which are in direct contact with each other within a fuel cell or battery.

Generally, it will be understood by persons skilled in the art that the term "fuel cell" denotes a power generating electrochemical device to which reactants (fuel plus oxidant) are fed continually to meet demand. The term "battery" will be generally understood to mean a power generating electrochemical system that is self-contained and which receives no continual feed of reactants to meet demand, but which can become electrochemically depleted. Batteries may, of course, be replenished by electrical charging. It is not the purpose of this document to provide new definitions of "fuel cell" and "battery", but it is within the scope of the present invention for a battery to have mobile or mobilisable reactants contained within it.

A conventional fuel cell or battery consists of two electrodes sandwiched around an electrolyte which serves to keep the chemical reactants physically separated from each other. In one common type of fuel cell the reactants are hydrogen and oxygen. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat. In such a type of fuel cell, hydrogen fuel is fed to the anode of the fuel cell.

Oxygen, or air, is fed to the fuel cell in the region of the cathode. At the anode, hydrogen atoms are split into protons and electrons, usually with the assistance of a catalyst. The protons pass through the electrolyte, which is an ionic conductor but which has a very high resistance to passage of electrons and can therefore be regarded as an electronic insulator. The electrons therefore take an external path to the cathode and can be passed through a load to perform useful work before reaching the cathode. At the cathode, protons that have migrated through the electrolyte are combined with oxygen and electrons to form water.

Since fuel cells rely on electrochemistry rather than thermal combustion for useful energy conversion, operating temperatures and conversion efficiencies are higher so that emissions from fuel cell systems are very much smaller than emissions from even the cleanest fuel combustion systems. These are two reasons why fuel cells are attractive. However, the current high cost of fuel cells is outweighed by the relatively cheap cost of producing electricity by combustion. Although fuel cells offer additional advantages such as low noise and wide load capability, the major effort in current fuel cell technology is aimed at developing cheaper systems that compete with conventional power-generating systems on the basis of cost, weight and volume.

The majority of work reported in fuel cell technology is based on conventional arrangements as described above in which separate feeds of fuel and oxidant are delivered to different compartments of the

fuel cell. However, a very small minority of workers have investigated the possibilities, the majority of which are described below, of using mixed reactants. Although direct reaction between mixed reactants is thermodynamically favourable, it can be effectively suppressed or prevented for a number of reasons, which can be exploited by the cell designer: For example, reaction may be effectively prevented by a high activation energy for the direct reaction and/or by slow kinetics for the reaction and/or by slow diffusion of species. By adopting selectively catalytic electrodes or other selective approaches, a reduction reaction can be promoted at the cathode and an oxidation reaction at the anode, whilst the degree of parasitic reaction in the reactant mixture is negligible.

Early work in the field of mixed reactant fuel cells was reported by Charles Eyraud, Janine Lenoir and Michel Géry in Seánce, 13 March 1961. The single cell reported in this document uses a porous alumina membrane having water molecules adsorbed thereon which, under certain conditions of temperature and pressure, can be made to act as a film electrolyte. The cathode is a porous metal sheet of copper or nickel, for example. The anode is a vacuum-deposited layer of platinum or palladium. It is reported that, in humid air (i.e. no fuel), the oxidation of the nickel manifests itself in a potential difference across the electrodes of a porous Ni-Al<sub>2</sub>O<sub>3</sub>-Pd element. With fuel incorporated in the feed gas mixture, the performance of this arrangement is limited by the diffusion characteristics of the fuel and oxidant mixture

through the porous alumina element. The addition of an ionisable constituent such as ammonia into the alumina or into the gaseous mixture as a means of enhancing the ionic conductivity of the fixed water film electrolyte adsorbed in the porous alumina was contemplated. None of these concepts seem to have been developed into a worthwhile product.

C.K. Dyer in Nature, Volume 343, (1990), pages 547-548, describes a thin-film electrochemical device for energy conversion. Dyer's device is a solid electrolyte fuel cell capable of operating with a mixture of an oxidant and a fuel. It includes a permeable catalytic electrode and an impermeable catalytic electrode, the two electrodes being separated by an electron insulating but ion-conducting, gas permeable solid electrolyte. This solid electrolyte fuel cell operates on a gas fuel/oxidant mixture. The mixture is supplied to only one electrode and diffuses to the other electrode through the porous electrolyte. A concentration gradient is established through differential diffusional migration through the solid electrolyte. The device is described in single cell form only.

Moseley and Williams in Nature, Volume 346, (1990), page 23, report use of Au/Pt electrodes in a sensor device for sensing reducing gases. In their system, atmospheric water adsorption on the surface of a substrate separating the electrodes acts as a fixed film electrolyte. They also claim that the platinum electrode can support electrochemical combustion of a target gas such as carbon monoxide. Their device exhibits the

convenient attributes of operating at room temperature and functioning without the need to separate the analyte (fuel) gas from the oxidant. It is emphasised that this device operates as a sensor and its use for power generation was not contemplated.

W. van Gool in Philips Res. Repts., Volume 20, (1965), pages 81 to 93, discusses the possible use of surface migration in fuel cells and heterogeneous catalysis. In one disclosed arrangement, both electrodes are in contact with a mixture of fuel gas and oxygen, ions migrate across a substrate surface between the electrodes and selective chemisorption is used to achieve separation. This type of fuel cell arrangement is inherently unsuitable for power generation because of the high resistance afforded by the electrolyte geometry and is generally applicable only to sensor applications. Selective electrodes, particularly operating by selective chemisorption, are seen as useful in this type of fuel cell arrangement.

A review of solid oxide fuel cells operating on uniform mixtures of fuel and air appears in Solid State Ionics, Volume 82, (1995), pages 1-4.

Hibino and Iwahara describe a simplified solid oxide fuel cell system using partial oxidation of methane in Chemistry Letters, (1993), pages 1131-1134. An alternative fuel cell system is proposed which works at high temperatures and uses a methane plus air mixture as an energy source. A  $Y_2O_3$ -doped zirconia (YSZ) disc is used as a solid electrolyte. A nickel-YSZ cermet (80:20 wt%) was sintered on one surface of the solid electrolyte

disc at 1400°C, and then Au metal was applied to the other face of the solid electrolyte disc at 900°C. These electrodes are reported to be sufficiently porous to allow the ambient fuel plus air mixture to diffuse through them. Early designs based on this system were acknowledged as being unsatisfactory in terms of electrical power output.

More recently (Science, Volume 288, (2000), pages 2031-2033), Hibino has reported a low-operating temperature solid oxide fuel cell using a hydrocarbon-air mixture but using samaria-doped ceria (SDC) as the solid electrolyte. SDC is reported to have a much higher ionic conduction than YSZ in an oxidising atmosphere. Also, this system uses no precious metals in the electrodes, so fabrication costs are relatively low.

In similar vein, Gödickemeier et al. report in the Proceedings of 192nd Meeting of Electrochem. Soc. and the 48th Meeting of the Int. Soc. of Electrochem - Paris, France, 1997, solid oxide fuel cells with reaction-selective electrodes. They report an arrangement in which solid oxide fuel cells are operated in uniform mixtures of fuel gas and air. The voltage is generated between an anode which is selective for the oxidation of the fuel and a cathode on which only the reduction of oxygen can occur. In the case where the fuel gas is methane, the cathode is inert to the combustion of methane.

In Fuel Cells, Modern Processes for the Electrochemical Production of Energy, Wolf Vielstich, Institute für Physikalische Chemie der Universität Bonn



(Translated by D.J.G.Ives, Birkbeck College, University of London, Wiley-Interscience ISBN 0 471 906956), a cell is described on pages 374 and 375 as being a radiolytically regenerated oxyhydrogen cell. Water is decomposed to hydrogen and oxygen by means of a chemical nuclear reactor. The product gas, a mixture of hydrogen and oxygen, is fed to an electrolytic cell comprising two gas-diffusion electrodes. The mixed fuel gas is first introduced to the cathode side of the cell and the oxygen concentration is decreased as a result of selective reaction. The residual gas, rich in hydrogen, is then fed to the anode side of the cell. In this arrangement, the utilisation of the mixed fuel occurs in a two-step process. A liquid electrolyte is constrained between the electrodes, while the reactant gases are supplied to the external surfaces of the electrodes.

Zhu et al, Journal of Power Sources, Volume 79, (1999), pages 30-36, describes so-called "non-conventional" fuel cell systems, including single chamber systems operating on mixed reactants. A conventional solid electrolyte is used and doping is discussed as a means of tailoring the electrical conductivity and other properties of the electrolyte and/or electrodes to obtain the required function.

One of the key advantages that can be attributed to each of the mixed reactant systems discussed above is that use of mixed reactants allows complex manifolding to be eliminated. There is no longer any need for convoluted passages to be constructed to deliver the separate fuel and oxidant feeds to respective chambers in

the fuel cell. Hence, the problematic sealing requirements of the fuel cell are eased. Additionally, an arrangement with lessened sealing demands and no manifolding is not so wasteful of space as a conventional fuel cell. An infrastructure is still required to move fuel plus oxidant from one place to another within or across the cell but, generally speaking, use of a mixed reactant system allows greater versatility in cell design. The mixed reactant technology can be applied to gas mixtures generated from radiolytic, electrolytic or photolytic systems. An example of a system exploiting spent gas generated radiolytically is discussed above.

The disadvantages of mixed reactant fuel cells compared to their conventional counterparts are that they generally deliver lower performance in terms of fuel efficiency and cell voltage (parasitic fuel-oxidant reactions). Problems associated with parasitic reactions could be overcome by development of better selective electrodes. With conventional electrode materials, the efficiency of mixed reactant fuel cells will be inferior to that of a conventional system in which the fuel and oxidant are maintained in separate feeds. However, other performance measures such as cost and power-density may be significantly enhanced. A concern with mixed reactant fuel cells is that certain reactant mixtures have an attendant risk of explosion. However as discussed above, mixed reactants do not necessarily undergo reaction simply because it is thermodynamically favourable.

Another limitation of known fuel cells is that electrochemical reaction only occurs at an interface

between three phases. In other words, electrochemical reaction is limited to sites on the catalyst where reactant and electrolyte meet together. This latter problem is not only a limitation in mixed reactant fuel cells, but is also a disadvantage of conventional fuel cells.

It is therefore an object of the present invention to provide a fuel cell or battery that ameliorates the disadvantages outlined above. In particular, it is an object of the present invention to provide a fuel cell or battery that eliminates complex manifolding and reduces problems associated with providing effective sealing. It is also an object of the present invention to provide a fuel cell or battery that makes more effective use of the space it occupies. It is yet another object of the present invention to provide a fuel cell or battery that is versatile in its use or applicability and which has the capability of using mixed fuel and oxidant as reactants that are readily available from the environment, or which has the capability to use gases produced in radiolytic, electrolytic or photolytic systems. It is a still further object of the present invention to compensate for less than perfect utilisation of fuel by boosting overall performance. It is yet another object of the present invention to provide a fuel cell or battery that is capable of delivering high power levels on demand.

In a first aspect, the invention is a fuel cell or battery for providing useful electrical power by electrochemical means, comprising:

10

at least one cell;

at least one anode and at least one cathode within said cell, and

ion-conducting electrolyte means for transporting  
5 ions between the electrodes;  
characterised in that:

said electrodes are porous and in that means are  
provided for causing hydrodynamic flow of a mixture of at  
least fuel and oxidant through the body of said  
10 electrodes.

It is important that the fuel and oxidant is present  
in a mixed form. Preferably, the mixture is a fluid,  
which term is used to include liquids, gases, solutions  
15 and even plasmas. The components of the mixture  
preferably have high diffusivity within each other.

In an especially preferred form of the invention,  
the electrolyte means is or forms part of the mixture.

Most preferably, the fuel will be an oxidisable  
20 component in fluid form (as defined above). Oxidisable  
is used to denote that the fuel can donate electrons to  
form an alternative oxidation state. Examples of  
suitable fuels include hydrogen, hydrocarbons such as  
methane and propane, C<sub>1</sub>-C<sub>4</sub> alcohols, especially methanol  
25 and/or ethanol, sodium borohydride, ammonia, hydrazine  
and metal salts in molten or dissolved form.

Most preferably, the oxidant is a reducible  
component in fluid form. That is to say, the oxidant  
behaves as an electron acceptor. Examples of suitable  
30 oxidant materials include oxygen, air, hydrogen peroxide,

metal salts - especially metal salts containing oxygen such as chromate, vanadate, manganate or the like, and acids. The oxygen may be present in dissolved form, for example as dissolved oxygen in water, acid solution or  
5 dissolved in perfluorocarbon.

The electrolyte may be a solid electrolyte (immobile), or may be a component in fluid form if it is or forms part of the mixture. The electrolyte has ionic/electronic transport capabilities such that it  
10 conducts ions in preference to electrons. Suitable materials for the solid form electrolyte include currently available materials known in the art such as sulphonated and/or non-sulphonated polymeric membranes, inorganic ionic carriers such as yttria stabilised  
15 zirconia (YSZ), ceria stabilised zirconia (CSZ), india stabilised zirconia (ISZ), ceria stabilised gadolinia (GSG) and silver iodide. The solid electrolyte may be supported on a porous matrix, or the solid material may be the electrolyte itself. Examples of fluid electrolyte  
20 include water and aqueous systems, acidified perfluorocarbons, plasma, molten salts, acids and alkalis.

It is possible that the fuel or oxidant can create or behave as an electrolyte. In other words, if an  
25 electrolyte is present in the mixture, it does not have to be a discrete component in the mixture. Similarly, neither do the fuel and oxidant have to be discrete components in the mixture. However, it is vital that the mixture has at least dual functionality in that the  
30 functions of oxidant and fuel must be attributable to it.

The term "electrode" in this document will be understood as including electrocatalysts and an electronically conducting medium into or onto which the electrocatalyst is incorporated, or which is the electrocatalyst itself.

In its especially preferred form, in which the electrolyte means is or forms a part of the mixture, a key advantage that the present invention has over conventional fuel cells, as well as over mixed reactant systems of the types described above, is that the incorporation of electrolyte functionality in the reactant mixture vastly increases the effective active surface at the electrode. Conventionally, the way of increasing the active surface area of an electrode has been to provide increasingly small electrocatalyst particles. By causing the reactant mixture with its triple functionality to pass through the body of a porous electrode, the present invention effectively maximises the active surface of the electrode.

Also, conventional solid electrolytes are expensive and the present invention therefore offers the possibility of omitting one of the costly parts of the fuel cell. Hence, manufacturing costs can be decreased. Furthermore, the solid electrolyte employed in conventional fuel cells requires careful water management. Hydrated polymeric electrolyte membranes are, for example, susceptible to drying out or flooding if the water management is not optimised. Fluid electrolytes generally have higher conductivity than solid electrolytes. Additionally, fluid electrolytes can

be agitated to enhance ionic transport still further. Thus, it can be seen that there are many advantages in constructing a fuel cell which dispenses with the traditional electrolyte and its attendant shortcomings.

5           Another advantage is that use can be made of environmental products that already comprise a mixture of fuel plus oxidant, for example land-fill gas comprising methane plus air.

10           Although mass transport will be limited in non-fluid systems, it is recognised that some applications for the fuel cells according to the present invention will benefit from using a constrained mixture. For example, in the field of miniature fuel cells and/or solid state fuel cells that are intended for use as battery  
15           replacements, replenishment of the mixture as a cartridge/cassette or other readily-manipulated form would be advantageous. Such replenishment could be akin to replacing an exhausted ink cartridge in a printer apparatus or the like, or to refuelling a cigarette  
20           lighter or heated hair curling tongs.

          Replenishment of the fuel cell or battery is not restricted to the example given above which describes replenishment of the mixture by physical means. Replenishment of the mixture could alternatively be by  
25           thermal, chemical or electrical means. It is also within the scope of the present invention for individual constituents of the mixture to be regenerated or renewed. Such replenishment may be by physical, thermal, chemical or electrical means.

30           The operating temperature range of fuel cells in

accordance with the present invention may be from 0°C up to 1000°C or higher. Those systems which use a plasma component in the mixture will be difficult to categorise in terms of operating temperature because it is difficult to measure plasma temperatures.

The fuel cell or battery according to the present invention may include means, such as baffles or a stirrer, for generating turbulence within the system to enhance species transport to and from the electrodes. One or more of the electrodes may be capable of adsorbing or otherwise storing either fuel or oxidant species.

Preferably, a high activation energy for reaction between the reactants is utilised to provide stability against self-discharge of the fuel cell or battery. Alternatively, or in addition, slow kinetics for reaction between the reactants can be utilised to provide stability against self-discharge. Also, slow kinetics for diffusion of the reactants can be utilised to provide stability against self-discharge.

An oxygen-carrying liquid (such as a perfluorocarbon) may be used to dissolve oxygen or to co-dissolve fuel and oxygen. The oxidant component of the fuel cell or battery may then be recharged by dissolution of a gas (such as oxygen) in a suitable liquid, such as a perfluorocarbon.

The present invention also contemplates a fuel cell or battery operating on a single supply of a stable combination of reactants that are or are contained in immiscible or partially immiscible phases. An example of such an arrangement would be a reactant/electrolyte means



mixture comprised of a stable emulsion. The fuel cell or battery according to the present invention may operate on a single supply of a combination of reactants that are or are contained in immiscible or partially immiscible phases which spontaneously segregate within the device. Alternatively, the fuel cell or battery may operate on separate supplies of oxidant and reductant that are or are contained in immiscible or partially immiscible phases that nevertheless come into contact within the device in the presence of electrolyte means which may, optionally, be combined with at least one of the separate supplies of oxidant and reductant. As previously mentioned, the oxidant and/or reductant may have electrolyte functionality so that a separate electrolyte component is not required.

Turbulence can be used to increase the contact between the immiscible or partially immiscible phases. Preferably, the electrolyte is present to an appreciable degree in both phases because, as discussed above, the electrochemical reaction can only occur at the three-phase catalyst/electrolyte/reactant interface. Hence, if one of the immiscible or partially immiscible phases is electrolyte deficient, the opportunities for electrochemical reaction will be limited and the performance of the fuel cell or battery will be compromised. Again, turbulence can be used to increase the surface area of contact between an electrolyte deficient phase and an electrolyte rich phase and the relevant cell electrode.

The fuel cell or battery according to the present

invention may utilise the electrode materials both as a surface for the primary cell reactions and as reactants for secondary cell reactions which provide the cell with additional output voltage and/or higher inherent energy density. The fuel cell or battery according to the present invention may also utilise the NEMCA (Non-faradaic Electrochemical Modification of Catalytic Activity) or similar effects to enhance the stability of the mixture when the device is not generating electricity. The NEMCA effect is a recognition that the activity of an electrocatalyst is modified by its surface charge.

The fuel cell or battery according to the present invention may include a supply of reactants containing a component capable of disproportionation. Such a system may optionally be rechargeable. For example, the reactant may include carbon monoxide which disproportionates to carbon and carbon dioxide, which can be regenerated to carbon monoxide by heating. Another example is a solution of manganese ions, in which the disproportionating component is also the electrolyte.

The porosity of the electrodes is such that flow of the mixture occurs through the bulk of the electrode material and is available for electrochemical reaction. The pores are "open" or "connected", by which is meant that every pore connected to the outer surface of the electrode. Typical pore dimensions will range for 5 $\mu$ m to 5mm.

Suitable materials for the electrodes may be sintered powder, foam, powder compacts, mesh, woven or

non-woven materials, perforated sheets, assemblies of tubes or the like, all with with deposited electrocatalysts if they are not themselves electrocatalysts, but the invention is not limited to such materials.

The predominant flow in this arrangement is through the body of the electrodes, rather than flow past the surface of the electrodes. The flow is predominantly hydrodynamic rather than diffusive, by which is meant that bulk movement or flow of the mixture is caused by an external impetus rather than by diffusion through the bulk of the electrodes. The external impetus may be gravity or the mixture may be forced to flow by a pump or applied vacuum pressure, etc. It is also important that the flow of the mixture through the body of the electrodes is such that the mixture is available for electrochemical reaction.

The electrodes may be disposed in an orientation transverse to the direction of flow of the mixture. In this arrangement, the mixture may flow first through an anode or cathode and subsequently through an electrode of opposite polarity, i.e. through a cathode or anode, respectively. A porous separator or electrolyte may be interposed between the electrodes. A stack of electrodes of alternating polarity may be provided and the external connections to these electrodes may be organised such that they form a stack of cells in series or in parallel, as required.

In one preferred embodiment of this arrangement, the electrodes are simply mounted within conduit means such

as a pipe, such that the flow of mixture passes through them. A single cell version of this embodiment simply requires an anode and cathode mesh to be inserted across the conduit means and for each to be connected to an external circuit. The electrodes must support selective catalysts and, even though the mixture flowing through the cell may include an electrolyte or may have electrolyte functionality, a porous solid electrolyte or separator may be interposed between the two electrodes.

The electrodes should preferably be placed in the correct position with regard to the flow direction of the mixture. This condition is essential if the flow rate is greater than the ionic diffusion rate, but is preferable in any case. In other words, the electrode that generates the mobile ionic species should preferably be placed upstream of the electrode that consumes the mobile ionic species. Thus, for example, in a hydrogen fuel cell, the anode should be placed upstream of the cathode because it is the anode which generates the mobile hydrogen ions (protons).

The single cell described above may be readily extended to a stack of electrodes connected in parallel. Preferably, anodes and cathodes will alternate along the length of the conduit means, all separated either by a small gap or by a functionally inert porous membrane. If the mixture itself provides electrolyte functionality, the porous membranes do not require electrolyte capability although there may be additional advantage in utilising electrolyte membrane as such a separator. In such an example the structure will be of the type

A/E/C/E/A/E/.../C, where A is an anode, C is a cathode, and E is either a porous membrane (which may be functionally inert or may have electrolyte capability) or a small gap. E must have electrolyte capability if there  
5 is no electrolyte in the mixture.

In the case of a series stack, the corresponding preferred structure will be of the type A/E/CA/E/CA/E.../C. CA pairs must be electrically connected and may be in direct physical contact or be  
10 connected by a porous electrical interconnect. As described above, care must be taken with the flow direction and with the electrode efficiencies; it is preferable that the majority of mobile ions generated at the anode should be consumed at the first cathode through  
15 which they pass. Secondly, to inhibit ionic short-circuiting between cells it may be advantageous to adjust cell separation distances or mixture flow rate.

In an alternative arrangement, the electrodes may be disposed in an orientation which is substantially parallel to the direction of flow of the mixture. In  
20 such an arrangement, a portion of the mixture flows through an anode, whilst the remainder flows through a cathode. If only a single anode and a single cathode is disposed in the mixture flowpath, the utilisation of the electrochemical potential of the mixture will be poor  
25 because some of the mixture will only have been exposed to anodic conditions, whilst the remainder of the mixture will only have been exposed to cathodic conditions. One way to improve reactant utilization is to dispose at  
30 least one more pair of electrodes downstream of the first

pair, with opposed polarities in corresponding portions of the flowpath. In other words, the second anode will be disposed downstream of the first cathode and the second cathode will be disposed downstream of the first anode.

The arrangement described above in which the electrodes are disposed substantially parallel to the direction of flow of the mixture need not be limited to respective pairs of electrodes at given points in the flowpath. More complex electrode arrays are possible across the flowpath of the mixture, for example a series connected array of multiple cells. The limitation of this approach is determined by the closest proximity of anodes and cathodes that can be realised without serious risk of short-circuiting. Separators between the electrodes will need to extend sufficiently far into the mixture flowpath that surface migration of charged species across the separators is prevented.

In a second aspect the invention is a fuel cell or battery for providing useful electrical power by electrochemical means, comprising:

at least one cell;

at least one anode and at least one cathode within said cell, and

an alkaline electrolyte for transporting ions between the electrodes; characterised in that:

said electrodes are porous and in that means are provided for causing hydrodynamic flow of a mixture of at least fuel and oxidant through the body of said

electrodes wherein said fuel is carbon or a carbonaceous species.

Hitherto, it has been thought that it is not possible to operate a low temperature fuel cell, such as those based on proton exchange membranes or alkaline electrolytes, with a conventional platinum anode catalyst in the presence of certain carbonaceous species because the species will rapidly poison the platinum catalyst and severely degrade its performance. However, in accordance with the present invention, it has now proved possible to operate an alkaline fuel cell directly on a hydrocarbon fuel, such as methanol, or a CO/CO<sub>2</sub>-containing fuel with a simple platinum catalyst anode for extended periods without significant degradation provided that electrolyte concentration is maintained. Without wishing to be bound by theory, it is believed that the mechanism which allows such operation without poisoning of the platinum catalyst is the effective scrubbing of the carbonaceous species by the electrolyte. The advantage brought to this concept by the present invention is that the electrolyte may be or may form mixture and may therefore be fed to the cell at concentrations which permit continuous operation without catalyst poisoning.

In addition, the continuous introduction of an oxidant, such as air, allows operation of such an alkaline fuel cell to be maintained when an air cathode (typically based on manganese or nickel) is immersed directly in the mixture.

In a third aspect the invention is a fuel cell or

battery for providing useful electrical power by electrochemical means, comprising:

at least one cell;

at least one anode and at least one cathode within  
5 said cell, and

ion-conducting electrolyte means for transporting ions between the electrodes;

characterised in that:

said electrodes are porous and in that means are  
10 provided for causing hydrodynamic flow of a mixture of at least fuel and oxidant through the body of said electrodes, wherein said electrodes have electrocatalysts associated therewith which are selective by virtue of their electric potential.

15

The phenomenon whereby catalysts can be rendered selective by virtue of their electric potential rather than, or in addition to, their chemical or physical nature is well-known as the NEMCA (Non-faradaic  
20 Electrochemical Modification of Catalytic Activity) effect. The invention uses the same NEMCA catalyst for both anode and cathode in a single chamber fuel cell. When at a relatively positive potential, the catalyst favours the reduction reaction, whilst at a relatively  
25 negative potential it favours the oxidation reaction. Once the fuel cell is operating, the electrochemical reactions will tend to maintain the bias on the respective electrodes, and hence their selectivity. The bias may be established initially through positive  
30 feedback of a random instability, or by brief application



of an external potential.

The advantage of this arrangement is that the polarity may be reversed during operation, by the brief application of an external potential, such that the anode becomes the cathode and vice versa. The external potential may be applied, for example, by an external power source, or by use of a capacitor charged by the fuel cell itself. The benefit is that the performance of the fuel cell can be significantly improved, which is manifested as higher current density, cell voltage and improved fuel utilisation.

Currently fuel cells are subject to two disadvantages which affect their performance that can be overcome by this aspect of the present invention. Firstly, reactants become depleted near the electrodes. Secondly, catalysts become poisoned during operation, such that their initial performance is reduced very significantly after current has been flowing a relatively short time, perhaps as little as a few minutes. Reversing the polarity of the fuel cell on a regular basis can relieve both of the above problems and yield improved current and voltage characteristics by reducing power losses due to cell polarisation.

Under normal operation in any fuel cell, fuel locally present at the anode is oxidised while oxidant locally present at the cathode is reduced, causing both these reactant species to become depleted at their respective electrodes, with resultant cell performance degradation over time. In a mixed reactant fuel cell as described in this specification, as well as the foregoing

processes, non-reacting oxidant will be locally present at the anode and may possibly build up. Similarly, there will be non-reacting fuel present at the cathode which may also accumulate. However, as soon as a reversal of polarity is imposed, these local concentrations of fuel and oxidant are able to engage in the electrochemical reaction, thereby significantly improving instantaneous cell performance. Simultaneously, i.e. as soon as electrode polarity has been reversed, the local concentration of previously depleted reactant is provided with an opportunity to recover. By regularly switching electrode polarity at an optimum rate suited to the geometry and nature of the mixed reactant cell, it is possible to maintain an overall cell performance that approaches its peak instantaneous performance.

In situations in which an electrode catalyst may become poisoned by one or more chemical species, reversing the polarity of the electrode can provide time for the catalyst to recover. Recovery may occur, for example, by release/diffusion of poisoning species from the catalyst surface or by reaction of those species. The rate of recovery may also be enhanced by the local change in polarity of the catalyst. One example of a cell in which catalyst recovery may be particularly beneficial is the direct methanol fuel cell, in which a platinum anode is rapidly poisoned by carbonaceous species. This type of cell is characterised by a high instantaneous power density when the cell is first operated, but this rapidly tails off as anode poisoning progresses. Changes in electrode polarisation are

therefore important in limiting the extent of poisoning.

Fuel cells have been suggested as an efficient means to generate heat and electrical power as a replacement for a conventional gas or oil-fired boiler or furnace. A number of such systems have been demonstrated based upon both polymer electrolyte membrane (PEM) fuel cells and solid oxide fuel cells (SOFCs). A common problem with these systems is the level of complexity involved, which has already been discussed above, and the consequent high cost of the systems. A second common problem is the extended period of time taken to start up these fuel cell systems before they can generate electricity. For SOFC based systems, the start up time is prolonged because of the risk of thermal stresses to the ceramic material. For PEM based systems, the prolonged startup time is due to the heat-up time of the associated fuel reformer. Without a high volume of manufacture it is unlikely that such fuel cell-based systems will achieve a sufficiently low manufacturing cost and selling price to capture a significant market share. Without fast response/start-up time, it is also unlikely that such systems will offer sufficiently attractive performance characteristics to displace conventional systems.

It is therefore an object of the invention to overcome the above problems by providing a novel low-cost fuel cell with the capability of rapid response/start-up.

According to its fourth aspect, the invention is a fuel cell or battery for providing useful electrical power by electrochemical means, comprising:

at least one cell;

at least one anode and at least one cathode within said cell, and

ion-conducting electrolyte means for transporting ions between the electrodes;

5 characterised in that:

fuel and oxidant are present as a gaseous mixture, and in that a gas burner is provided within the cell.

10 The gas burner may be a substantially porous matrix electrolyte layer or block of particles, fibres or layer(s) coated on one side with a suitable anodic electrocatalyst and coated on the other with a suitable cathodic electrocatalyst. The fuel/oxidant gas mixture is passed through one or more such matrices and burned, 15 thereby heating the matrix to a sufficient temperature to enable it to function as an electrolyte. Burning of the gas may be done conventionally with a flame or optionally with the aid of catalyst. Multiple layers of electrocatalyst-coated matrix may optionally be stacked 20 together with intermediate layers of a porous electrically conductive material so that electrical power can be more readily drawn from the fuel cell.

The electrocatalysts are chosen such that the anode is substantially selective toward fuel oxidation and the 25 cathode is substantially selective toward oxygen reduction.

This variant of the present invention solves the problems of cost and response speed associated with existing fuel cell-based power generators because: the 30 porous electrolyte matrix is highly resistant to thermal

shock; and the invention acts as a fuel burner element that can be designed specifically to replace directly the existing fuel burner element in a conventional gas boiler.

5           There are three main applications for fuel cells or batteries in accordance with the present invention. Firstly, they may be used in automotive applications, ultimately for installation on board vehicles to replace internal combustion engines. Already, some hybrid  
10 systems are in practical use, where an engine burning fossil fuel is supplemented by a fuel cell. Typically, hydrogen fuel cells are used - the hydrogen may be stored on board the vehicle or may be formed by a reformer. A  
15 liquid fuel such as methanol could be used instead to feed a mixed reactant system as described here. This has the advantage of delivering a higher peak current. Currently, however, fuel cells are unable to compete with internal combustion engines in terms of cost per unit power. Typically, for an internal combustion engine, the  
20 power costs \$30 to \$40 per kW. Size considerations must also be taken into account, since fuel cells are unlikely to be adopted as internal combustion engine replacements if bulky fuel storage and fluid management systems are required that occupy more space than current  
25 arrangements.

          Another application for fuel cells in accordance with the present invention will be for stationary systems, such as combined heat and power generation. Infrastructure already exists for distributing power  
30 generated centrally, but distributed heat is relatively

rare. One advantage of fuel cells is that they are equally efficient when scaled down, so they have potential for use in residential applications for generating heat and power in combination.

5           Another application for fuel cells according to the present invention is for replacement or support of conventional batteries. As discussed above, fuel cells in accordance with the present invention can be recharged mechanically rather than chemically or electrically, so  
10 this makes replenishment very quick. Also, the energy density of a system based on methanol, for example, is superior to that of conventional batteries and great potential is therefore seen for the application of fuel cells to portable electronics. This is particularly true  
15 when the manifolding requirement is removed, because the fuel cell can be made more compact. Also the oxidant is in the system so there is no need for an air electrode or exposure to air. Thus water management problems such as the drying out of the electrodes is thereby avoided.

20           The invention will now be particularly described by way of example only with reference to the drawings, in which:

Figure 1 is a schematic diagram of a conventional fuel cell;

25           Figure 2 is a schematic perspective view of a stacked cell according to a first aspect of the present invention;

Figure 3 is a schematic perspective view of the stacked cell connected in series;

30           Figure 4 is a schematic perspective view of the

stacked cell connected in parallel;

Figure 5 is a schematic perspective view of a stacked cell according to the first aspect of the invention with the electrodes disposed substantially parallel to the direction of flow of mixed reactants and connected in series;

Figure 6 is a schematic perspective view of a stacked cell according to the second aspect of the invention with the electrodes disposed substantially parallel to the direction of flow of mixed reactants and having electrodes connected in series and in parallel;

Figure 7 is a graph showing curves of voltage against current for a prototype three-chamber cell having the electrodes spaced 4cm apart;

Figure 8 is a graph of voltage against current comparing fuel cells using dissolved oxygen;

Figure 9 is a plot showing the variation in performance with different electrode spacings;

Figure 10 is a curve of voltage against current for a prototype stack of five anodes and cathodes;

Figure 11 is a plot of the power produced against time for the stack of Figure 7, and

Figure 12 is a graph comparing performance between a conventional fuel cell and a fuel cell constructed in accordance with the present invention.

Referring firstly to Figure 1, this shows schematically an arrangement for a conventional fuel cell 10, comprising an anode 11 and a cathode 12 separated by an electrolyte medium 13 which permits passage of ions

but which prohibits transfer of electrons. External to the chamber containing the electrolyte medium 13 are respective anode and cathode gas spaces 21, 22. Anode gas space 21 has an inlet 31 for receiving a feed stream of an oxidant, such as oxygen. Cathode gas space 22 has an inlet 32 for receiving a feed stream of a fuel, such as hydrogen, and an outlet 42 for removing unused fuel and by-products of the electrochemical reaction.

The respective gas spaces and feed streams must be isolated from each other and, although it is not clear from the schematic representation of Figure 1, a fuel cell assembly constructed according to conventional principles can involve complex and convoluted manifolding. The sealing requirements are demanding and much potentially useful space is occupied by components that do not contribute to the power output of the cell.

Figure 2 is a schematic perspective view of a fuel cell stack 50 according to the second aspect of the invention. The cell stack 50 is an assembly of alternating anodes 51 and cathodes 52 mounted transversely within a pipe 54. Preferably, the electrodes occupy substantially the entire cross-sectional area of the pipe 54, such that bulk of the flow of mixture 53 passes through them with very little, if any, of the mixture passing the electrode edges. This ensures maximum utilisation of the mixture on a single pass. The electrodes are macroporous, by which is meant that they have open pores of sufficient dimensions that hydrodynamic mass transport through the bulk electrode material is predominant over transport by diffusion.



Figure 2 shows an arrangement in which the electrodes are connected in parallel, each of the anodes being connected to one another and each of the cathodes being connected to one another. Adjacent electrodes are separated by a small gap. The electrodes support selective catalysts and are placed in the correct position with regard to the flow direction of the mixture 53. That is to say, the anodes 51 at which the mobile ionic species are generated are positioned upstream of the cathodes, where the mobile ionic species are consumed.

Turning now to Figure 3, this shows a schematic perspective view of a stacked cell of similar configuration to that depicted in Figure 2, but with the macroporous electrodes connected in series. Identical reference numerals have been adopted to denote those features in Figure 3 which have already been described above in relation to Figure 2.

The electrodes are porous discs mounted transversely in the pipe 54 relative to the flow direction of the mixture 53. However, one major difference here is that adjacent electrodes are no longer separated by a small gap, but have porous separator membranes between them. The upstream electrode is an anode, which is separated from its downstream neighbouring electrode (cathode 52) by a porous electrolyte membrane 55. The upstream cathode 52 is, in turn, separated from its downstream neighbouring electrode (second anode 51b) by a porous interconnect membrane 56. The porous interconnect membrane 56 is electrically conducting and ionically

insulating, in contrast to the porous electrolyte membrane 55 which is an electrical insulator but allows passage of mobile ions.

5 The structure is therefore of the type A/E/C/I/A/E/C/I/A/E.../C, where A is an anode, C is a cathode, I is an interconnect and E is an electrolyte.

10 In an alternative arrangement, the CA pairs may be electrically connected by being in physical contact. If the mixture 53 includes an electrolyte or otherwise displays electrolyte functionality, it is not essential for the porous membrane 55 to be an electrolyte. It could be functionally inert. In most circumstances, a functionally inert membrane 55 will be less costly than its electrolyte counterpart, but electrolyte  
15 functionality in the membrane 55 may improve cell performance. Hence, the choice of whether to use an electrolyte or a functionally inert material for the membrane 55 can be left to the cell designer provided that electrolyte functionality is present in the mixture.  
20 As described above, care must be taken with the flow direction and with the electrode efficiencies. It is important that the majority of mobile ions generated at an anode 51 should be consumed at the first cathode 52 through which they pass.

25 Figure 4, is a schematic perspective view of a stacked cell similar to that depicted in Figure 3, but with the macroporous electrodes connected in parallel. Again, common reference numerals have been used to denote features which have already been described above in  
30 relation to Figures 2 and 3.

The electrodes are porous discs mounted transversely in the pipe 54 relative to the flow direction of the mixture 53. The upstream electrode is an anode, which is separated from its downstream neighbouring electrode (cathode 52) by a porous electrolyte membrane 55. However, in this embodiment, the upstream cathode 52 is separated from its downstream neighbouring electrode (second anode 51b) by a porous separator 57 that is both electrically and ionically insulating.

The structure is therefore of the type A/E/C/S/A/E/C/S/A/E.../C, where A is an anode, C is a cathode, S is a separator and E is an electrolyte. As described above in relation to Figure 3, if the mixture 53 includes an electrolyte or otherwise displays electrolyte functionality, it is not essential for the porous membrane 55 to be an electrolyte. It may be functionally inert. In most circumstances, a functionally inert membrane 55 will be less costly than its electrolyte counterpart, but electrolyte functionality in the membrane 55 may improve cell performance. Hence, if the mixture has electrolyte functionality, the choice of whether to use an electrolyte or a functionally inert material for the membrane 55 is again left to the cell designer. As described above, care must be taken with the flow direction and with the electrode efficiencies. It is important that the majority of mobile ions generated at an anode 51 should be consumed at the first cathode 52 through which they pass.

Turning now to Figure 5, this shows an alternative

arrangement of stacked cell according to the second aspect of the invention, in which the macroporous electrodes are disposed substantially parallel to the direction of flow of the mixture 53. The electrodes are shown connected in series.

Again, common reference numerals have been used to denote features previously described in relation to Figures 2 to 4.

In the arrangement depicted in Figure 5, a portion of the mixture 53 flows through anodes 51, a portion flows through porous electrolyte membranes 55, whilst the remainder flows through cathodes 52. If the mixture passes through only one such assembly, the utilisation of the mixture will be poor because some of the mixture will only have been exposed to anodic conditions and some will only have been exposed to cathodic conditions. Hence, it is preferable to dispose at least one more electrode assembly downstream of the first one, with electrodes of opposite polarities in corresponding portions of the flowpath. In other words, anodes 51 will be positioned directly downstream cathodes and *vice versa*.

Such an arrangement is depicted in Figure 6, which shows a stacked cell according to the second aspect of the invention with the electrodes disposed substantially parallel to the direction of flow of mixed reactants and having electrodes connected in series and in parallel.

In the embodiments depicted in both Figures 5 and 6, if the mixture 53 includes an electrolyte or otherwise displays electrolyte functionality, it is not essential for the porous membrane 55 to be an electrolyte. It may

be functionally inert, which will probably mean that it is less costly than its electrolyte counterpart. However, electrolyte functionality in the membrane 55 may improve cell performance and is essential if there is no electrolyte functionality in the mixture 53.

### Experimental

Experiments were conducted using alkaline fuel cells. Current-voltage plots were obtained for fuel cells using methanol or sodium borohydride as fuel, potassium hydroxide as the electrolyte, and both gaseous and dissolved oxygen as the oxidant. The mixed reactant concept was tested in both static and in flow-through modes and in comparison against a 'conventional' separate reactant fuel cell mode.

The conventional cell, chosen as a control, was selected for ease of comparison with the fuel cell according to the present invention. The performance of the conventional cell, being a form of direct methanol cell, was very modest compared to the best gaseous-fuelled polymer electrolyte membrane fuel cells, but in keeping with the unoptimised design of the new mixed-reactant fuel cell.

Surprisingly, the mixed reactant cell gave out slightly more power than the conventional separate reaction cell. This was attributed to having fuel on both sides of the anode and to using oxygen dissolved in aqueous solution rather than in air.

Supplementary experiments demonstrated that the

'flow-through' fuel cell concept is also valid. A compact mixed-reactant fuel cell was constructed, comprising a stack of electrodes through which the mixture of fuel, oxidant and electrolyte was pumped. Surprisingly, it proved possible to obtain voltages higher than that for a single cell by electrically connecting cells in series. The reason for this is not yet fully understood.

A prototype fuel cell was set up by mounting electrodes between sections of perspex tubing of 5 cm external diameter. The cathode was manganese on a carbon support, on a nickel mesh, with a PTFE binder. The anode was platinum on a carbon support on a nickel mesh, again using a PTFE binder. These electrode materials, and the alkaline system in which they were used, were chosen primarily for their ready availability and for their ease of adaptation to a compact mixed-reactant format.

The fuel cell arrangement is depicted schematically above, showing electrodes sandwiched between perspex tubes. The tubes have inlets and outlets for gas and liquid, and were clamped together using o-ring seals.

Chamber 1 contained fuel, either  $\text{CH}_3\text{OH}$  (5% v/v) or  $\text{NaBH}_4$  (varying concentrations) dissolved in 1M KOH, which also acted as the electrolyte. Chamber 2 either contained electrolyte or a mixture of fuel and electrolyte. Chamber 3 contained either air,

electrolyte, or fuel and electrolyte. Oxygen was dissolved in the fuel or electrolyte by bubbling air through it.

Curves of current versus voltage were obtained by connecting a variable resistance across the fuel cell. After changing the resistance, the current and voltage were allowed to stabilise for one minute before measurement. In some experiments, particularly with small distances between the electrodes, I and V decreased rapidly with time.

The following passages summarise the experiments carried out and the cell performances obtained.

## 1. EXPERIMENTAL DATA

### 1.1 Initial Experiments

In the initial experiments, the electrodes were 4 cm apart. In the first experiment, cell 1 contained MeOH in KOH, cell 2 contained KOH and cell 3 contained air. In the second experiment MeOH in KOH was used as the electrolyte. Little difference was observed between the two experiments suggesting that the air cathode was selective towards  $O_2$  reduction and did not promote MeOH oxidation.

Towards the end of the set of experiments, KOH and MeOH was used in all three compartments, with  $O_2$  being bubbled through the cell in contact with the cathode. Results were significantly worse than when an air cathode was used, contrary to later observations. This is thought to arise from either the effect of the PTFE

backing on the cathode or, more likely, from some ageing effect - the performance of the electrodes appears to deteriorate with time.

In the first set of experiments, the initial open circuit voltage was 0.586V. After the first experiment the open circuit voltage was measured again and was 0.537V.

### 1.2 Second fuel cell experiment

The aim of this experiment was to compare fuel cells using dissolved oxygen, one of which had MeOH/KOH as the electrolyte, and the other of which had KOH as the electrolyte. Note that the ammeter was used on the A scale, so the resolution of the measurements is 0.001A.

### 1.3 Effect of varying electrode spacing

All three compartments contained 5%MeOH in 1M KOH, air bubbled through chamber 3. The first experiment (using fresh electrodes) used a 4cm gap between electrodes, and the open circuit voltage was 0.66V, 1 minute interval between readings. The second experiment used a 1.5cm gap between electrodes. After the set of experiments the cell was returned to open circuit conditions and the voltage was 0.537V increasing to 0.59V over 15 minutes.

Better performance was expected from the cell with a smaller spacing between electrodes because there would be less resistance to the flow of ions in the electrolyte between the electrodes. Instead, the dominant effect seems to be the consumption of fuel (or possibly



formation of  $K_2CO_3$  from the electrolyte) resulting in the power drawn from the cell decreasing over time - this caused the current drawn from the cell to decrease as the resistance decreased.

5

#### 1.4 First stack experiment

A stack of 5 anodes and 5 cathodes was assembled, fed by peristaltic pump, 1M KOH containing 0.104g  $NaBH_4$  in 300ml. Second cell up performed best (first electrodes possibly used before?) but performance fell off over time, as shown below. V open circuit was 0.874V.

10

15

With a resistance of 20 Ohms the voltage and current drawn from the cell were measured as a function of time, and a plot of the power produced against time is shown in Figure 8. After 42 minutes the flow rate was doubled from 0.5 rpm (0.032 ml/s) to 1.0 rpm (0.064 ml/s), causing the power output from the cell approximately to double also.

20

25

The open circuit voltage varied across the stack as shown in the table below. Fuel entered the stack at the bottom, so the gradual decrease in voltage going up through the stack can be explained by the consumption of the fuel by some back reaction. The poorer performance of the lowest cell may be due to the fact that all the other electrodes used in the experiment were fresh.

Electrode	Vopen circuit /V
5 (top)	0.303
4	0.455
3	0.616
2	0.812
1 (bottom)	0.350 (old?)

When the whole stack was connected in parallel an open circuit voltage of 0.476V was obtained, and the performance of the cell was poor. After this experiment the middle three cells were connected in parallel and the open circuit voltage was 0.288V, indicative of cell component degradation over time.

#### 1.5 Repeated experiment to test mixed reactant concept

Because of the suggestion that the cell was degrading over time, the experiments to test the concept of mixed reactants were repeated using fresh electrodes in each experiment. In a first experiment compartment 1 was filled with MeOH/KOH, cell 2 was filled with KOH and cell 3 was filled with air. In a second experiment using fresh solutions and electrodes mixed MeOH/KOH was used in each compartment and air was bubbled through the cathode compartment. As usual, measurements were made at 1 minute intervals.

This time the results showed (Figure 9) that the mixed reactant cell performed better than the separate compartments, due to methanol on both sides of the anode and/or the higher activity of O<sub>2</sub> in solution compared

with in air.

#### 1.6 Second stack experiment

The aims of this experiment were to test whether the same performance could be obtained from each cell in the stack, given an excess of fuel and a higher flow-rate, and to test the effect of connecting the individual cells in series and in parallel.

At 5 rpm, 19.08g of H<sub>2</sub>O were delivered in 60s, corresponding to a flow-rate of 0.32 cm<sup>3</sup>s<sup>-1</sup>.

Five cells were set up in a vertically-oriented stack. Initially, the lowest three cells were connected in series at 5rpm and the open circuit voltage obtained was 1.57 V. Each of the three cells was then connected separately, and they gave open circuit voltages of 0.79V (cell 1), 0.83V and 0.83V. When cells 1 and 2 were subsequently connected in series, an open circuit voltage of 1.20V was obtained. When the three were connected in series again, a voltage of 1.41V was obtained, again suggesting component deterioration with time.

The same three cells were also connected in parallel, and the current and voltage across a 20W resistor was measured, as shown below.

Cell	V/V	I/mA
1	0.60	16.4
2	0.69	18.7
3	0.70	18.9
1, 2 and 3 in parallel	0.755	20.3

Voltages and currents measured from the three cells independently, and connected in parallel.

In comparison, cell 3 was connected across a 40W resistor so that the voltage was 0.75V, similar to that from the three cells connected in parallel. The resulting current was 13.4mA. Again, although the three cells connected in parallel gave more power than any individual cell, the current flowing was not three times that produced by any one cell operating independently.

This non-ideal behaviour was attributed to the non-optimised construction of the cells and was not thought to be indicative of an unforeseen electrochemical effect.

## 2. ANALYSIS OF EXPERIMENTAL RESULTS

### 2.1 Effect of mixing reactants

Curves of voltage against current were measured for a reference cell containing  $\text{CH}_3\text{OH}/\text{KOH}$  in chamber 1,  $\text{KOH}$  in chamber 2, and air in chamber 3. V-I curves were also obtained for a cell containing  $\text{CH}_3\text{OH}/\text{KOH}$  with dissolved  $\text{O}_2$  in all three chambers. These classic polarisation results are shown in Figure 9.

Although the power from these alkaline fuel cells is low (as expected for direct-methanol), the above results demonstrate the present inventive concept - i.e. that power can be obtained from a mixed reactant cell. Furthermore, the mixed reactant cell performs better than the cell with separate fuel, electrolyte and oxidant ( $1.86 \text{ mA/cm}^2$  at 0.35 volts; peak power = 8.4 mW). This could be partly due to having methanol on both sides of the anode, but is also due to the fact that oxygen dissolved in water has a higher activity (0.25) than

oxygen in air (0.21) [more likely at open circuit than in a diffusion limited load mode]. These observations confirm that the enhanced performance is attributable to the increase in active surface area at each electrode due to operating in the all-liquid mode.

## 2.2 Effect of electrode spacing

The electrolyte in any fuel cell contributes a resistance to the electrochemical circuit. When a current is drawn from the cell this resistance results in a voltage drop, or polarisation, for the cell. Reducing electrolyte thickness, i.e. the spacing between electrodes results in a corresponding improvement in performance of the cell.

One benefit of the fuel cell according to the present invention is the elimination of one or more of the membranes/structures required to separate fuel from oxidant in the cell, so that electrodes can be placed closer together than in a standard cell. Experiments were performed using the mixed reactant ( $\text{CH}_3\text{OH}/\text{KOH}/\text{O}_2$ ) cell with the distance between electrodes being changed from 4 cm to approximately 1.5 mm to investigate this effect. The results are illustrated in Figure 6.

Surprisingly, decreasing the electrode spacing from 40mm to 1.5mm had minimal effect upon cell performance until a critical level of current was drawn. At this critical point, the power output from the cell decreased suddenly in a time-dependent way.

The region of minimal effect suggests that the performance of the test cell is dominated by factors

other than electrolyte resistance. These factors could for example, include electrode polarisation (i.e. the effectiveness of the chosen electrocatalysts).

5 The sudden drop-off in power at high current was attributed to reactant depletion within the small liquid volume between the electrodes. Although a contribution could also be due to  $K_2CO_3$  formation on the electrodes (i.e. blocking of the electrodes), this reaction between methanol and electrolyte should be more gradual than  
10 sudden.

Later experiments, replacing methanol with  $NaBH_4$  fuel, which does not react with the alkaline electrolyte, showed similar behaviour, indicating that  $K_2CO_3$  formation is not a significant factor in this case.

15 Further experiments utilising higher fuel concentrations and introducing a flow of the reactant mixture and electrolyte through the system according to the invention demonstrated that the sudden power drop-off could be avoided - i.e. that fuel depletion was the most  
20 likely cause.

### 2.3 Compact stack of fuel cells

A stack, consisting of 5 pairs of electrodes, was constructed by separating each electrode by a 1.5mm thick  
25 rubber gasket/spacer (annulus with four 'spokes' left in the 'wheel' to prevent adjacent electrodes from touching). Multiple pinholes were made in the electrodes to allow the reactant mixture to be slowly pumped through the stack using a peristaltic pump.

30

### 2.3.i Low fuel concentration & reactant flow-rate

Using  $\text{NaBH}_4$  as fuel at a concentration of 0.01 moles  $\text{dm}^{-3}$ , flowing through the stack at  $0.032 \text{ cm}^3\text{s}^{-1}$ , gave good results from the cells in the stack that were nearest to the reactant inlet, but the performance (voltage and current) of individual cells in the stack decreased steadily with position in the stack moving further from the inlet. This behaviour was observed under both open circuit conditions (i.e. no current drawn) and when current was drawn.

The open circuit behaviour demonstrated that a direct background reaction between fuel and oxidant is very likely to be occurring in which no electrons are transferred through an external circuit. This reaction could be happening at either electrode, but most likely at the platinum anode. It supports, very strongly, the importance of electrocatalyst selectivity which underlies the inventive fuel cell concept and demonstrates the concept very elegantly.

When power was drawn from cells in the stack, it decreased markedly with time until it levelled off to an approximate steady state. This suggested, as in the previous experiment described above, that fuel was being consumed at a faster rate than it was being replenished.

At 'steady-state', the power produced approximately doubled when the flow rate was doubled, again supporting the conclusion that performance was constrained by reactant supply.

### 2.3.ii High fuel concentration and reactant flow-rate

When  $\text{NaBH}_4$  fuel was used at a higher (5x) concentration (0.05 M) and much higher (10x) flow rate (0.32  $\text{cm}^3\text{s}^{-1}$ ), similar performance was obtained from each of the cells in the stack (previously, performance decreased along the stack in the direction of flow). This result confirmed that the effect of the background reaction between fuel and dissolved oxygen was much less significant than the electrochemical 'fuel cell' reaction between the two components. In addition, the proportionately higher power output of this experiment (1.58  $\text{mA}/\text{cm}^2$  at 0.70 volts; power = 13.2 mW across 20W resistance) compared to the lower flow rate and concentration (0.74  $\text{mA}/\text{cm}^2$  at 0.29 volts; power = 2.58 mW across 20W resistance) again reinforces the link between reactant flow and power output.

### 2.3.iii Parallel stack performance

Using the 5-cell stack of cells in the high concentration/high flow-rate mode described above, performance of individual cells was compared with multiple connected cells. The three central cells in the stack were connected electrically in both parallel and series modes.

From earlier analysis of the inventive fuel cell concept, parallel mode was originally considered to be the only practicable operating mode of the liquid electrolyte + fuel + oxidant combination. In parallel operation a fuel cell stack is normally expected to



operate as a single cell (i.e. single cell voltage) with a total cell area (and therefore total current) equivalent to the sum of the individual cells. In tests of the inventive cell stack, connecting anodes to anodes and cathodes to cathodes for the three central cells, an applied load of 20W gave considerably less than three times the individual cell performance (see table below).

Cell	V/volts	I/milliamps
1	0.60	16.4
2	0.69	18.7
3	0.70	18.9
1, 2 and 3 in parallel	0.755	20.3

Voltages and currents measured from the three cells independently, and connected in parallel.

The relative drop-off in performance of the parallel connected stack is not fully understood. One contributory factor may be higher electrical resistance of the parallel connected cells. To compare single cell and parallel performance more directly, the voltage of a single cell (cell 3) was raised by increasing the resistive load on the cell to 40W. With a new single cell voltage of 0.75V (similar to that from the three cells connected in parallel), the resulting current was 13.4mA. Again, although the three cells connected in parallel give more power than any individual cell, the current output of the parallel stack was still around half that anticipated. Further experiments are required to understand this behaviour.

#### 2.3.iv Series connected stack behaviour

Electrical connections to the three central cells were re-arranged to connect them in series. According to the initial analysis of the system, when connected in series, all but the outer electrodes in a stack of this type should short circuit and therefore give no more voltage or current than a single cell.

Surprisingly, as shown in the table below, when the three cells were connected in series a higher voltage (open circuit) was obtained than that for a single cell. Although the series voltage was less than the sum of the voltages from the three cells operating independently, the result suggests that the inventive system exhibits more complex behaviour than anticipated in the original concept. It may be possible to draw significant power from a simple series connected stack.

Cell	V/volts
1 (lowest)	0.79
2	0.83
3	0.83
1, 2 and 3 in series	1.57

Open circuit voltages from the three cells nearest the mixed reactant feed, and open circuit voltage from the same three cells connected in series.

Although the invention has been particularly described above with reference to specific embodiments, it will be understood by persons skilled in the art that variations and modifications are possible without departing from the scope of the claims which follow.

CLAIMS

1. A fuel cell or battery for providing useful electrical power by electrochemical means, comprising:

5 at least one cell;

at least one anode and at least one cathode within said cell, and

ion-conducting electrolyte means for transporting ions between the electrodes;

10 characterised in that:

said electrodes are porous and in that means are provided for causing hydrodynamic flow of a mixture of at least fuel and oxidant through the body of said electrodes.

15

2. A fuel cell or battery for providing useful electrical power by electrochemical means, comprising:

at least one cell;

20 at least one anode and at least one cathode within said cell, and

an alkaline electrolyte for transporting ions between the-electrodes;

characterised in that:

25 said electrodes are porous and in that means are provided for causing hydrodynamic flow of a mixture of at least fuel and oxidant through the body of said electrodes wherein said fuel is carbon or includes a carbonaceous species.

30 3. A fuel cell or battery for providing useful

electrical power by electrochemical means, comprising:

at least one cell;

at least one anode and at least one cathode within  
said cell, and

5 ion-conducting electrolyte means for transporting  
ions between the electrodes;

characterised in that:

said electrodes are porous and in that means are  
provided for causing hydrodynamic flow of a mixture of at  
10 least fuel and oxidant through the body of said  
electrodes, wherein said electrodes have electrocatalysts  
associated therewith which are selective by virtue of  
their electric potential.

15 4. A fuel cell or battery according to any preceding  
claim wherein the electrolyte means is or forms part of  
the mixture.

20 5. A fuel cell or battery for providing useful  
electrical power by electrochemical means, comprising:

at least one cell;

at least one anode and at least one cathode within  
said cell, and

25 ion-conducting electrolyte means for transporting  
ions between the electrodes;

characterised in that:

said electrodes are porous and in that means are  
provided for causing hydrodynamic flow of a mixture of  
fuel and oxidant through the body of said electrodes  
30 fuel, and further characterised in that a gas burner is

provided within the cell.

5 6. A fuel cell or battery according to any preceding claim wherein one or more of the reactants can be regenerated or renewed either electrically, thermally, chemically or physically.

10 7. A fuel cell or battery as claimed in any preceding claim wherein turbulence within the system is used to enhance species transport between the electrodes.

15 8. A fuel cell or battery as claimed in any preceding claim in which one or both of the electrodes is capable of adsorbing and storing either fuel or oxidant species.

20 9. A fuel cell or battery as claimed in any preceding claim wherein the interconnect is at least partially substituted by an electrically conductive and/or ionically insulating reactant mixture.

25 10. A fuel cell or battery as claimed in any preceding claim wherein a high activation energy for reaction between the reactants is utilised to provide stability against self-discharge of the device.

30 11. A fuel cell or battery as claimed in any preceding claim wherein slow kinetics for reaction between the reactants is utilised to provide stability against self-discharge of the device.

12. A fuel cell or battery as claimed in any preceding claim wherein slow kinetics for diffusion of the reactants is utilised to provide stability against self-discharge of the device.

5

13. A fuel cell or battery as claimed in any preceding claim wherein a diffusion barrier or partial barrier between the reactants is utilised to provide stability against self-discharge of the device.

10

14. A fuel cell or battery as claimed in any preceding claim wherein an oxygen carrying liquid is used to dissolve oxygen or to co-dissolve oxygen and at least one other constituent of the mixture.

15

15. A fuel cell or battery according to any preceding claim wherein recharging of the oxidant component is by dissolution of an oxygen-carrying gas in a suitable liquid.

20

16. A fuel cell or battery as claimed in any preceding claim operating on a supply of a stable combination of reactants that are or are contained in immiscible or partially immiscible phases.

25

17. A fuel cell or battery as claimed in claim 16 wherein the immiscible or partially immiscible phases spontaneously segregate within the device.

30

18. A fuel cell or battery as claimed in any preceding

claim operating on separate supplies of oxidant and reductant that are or are contained in immiscible or partially immiscible phases that come into contact within the device.

5

19. A fuel cell or battery as claimed in any preceding claim that utilises the electrode materials both as a surface for the primary cell reactions and as reactants for secondary cell reactions, thereby providing the overall cell with additional output voltage and/or higher inherent energy density.

10

20. A fuel cell or battery as claimed in any preceding claim having at least one catalyst utilising the NEMCA or similar effects to enhance the stability of the mixture when the device is not generating electricity.

15

21. A fuel cell or battery as claimed in any preceding claim wherein the mixture is or contains a component capable of disproportionation.

20

22. A fuel cell or battery as claimed in claim 21 that is rechargeable.

23. A fuel cell or battery as claimed in any preceding claim wherein the fuel is selected from hydrogen, hydrocarbons,  $C_1$ - $C_4$  alcohols, sodium boro-hydride, ammonia, hydrazine, and metal salts in molten or dissolved form.

25  
30

24. A fuel cell or battery as claimed in any preceding claim wherein the oxidant is selected from oxygen, air, hydrogen peroxide, metal salts, and acids.

5 25. A fuel cell or battery as claimed in claim 24 wherein the oxidant is selected from chromate, vanadate, manganate or a combination thereof.

10 26. A fuel cell or battery as claimed in any preceding claim wherein the electrolyte is a solid electrolyte selected from sulphonated and/or non-sulphonated polymeric membranes, inorganic ionic carriers including yttria stabilised zirconia (YSZ), ceria stabilised zirconia (CSZ), india stabilised zirconia (ISZ), ceria  
15 stabilised gadolinia (GSG) and silver iodide, or a fluid electrolyte selected from water and aqueous systems, acidified perfluorocarbons, plasma, molten salts, acids and alkalis.

20 27. A fuel cell or battery as claimed in any one of claims 1 to 4 or any one of claims 6 to 24 when dependent on claims 1 to 4, wherein the fuel and/or oxidant forms or behaves as an electrolyte.

25 28. A fuel cell or battery as claimed in any preceding claim wherein the electrodes are disposed in an orientation transverse to the direction of flow of the mixture.

30 29. A fuel cell or battery as claimed in claim 28



wherein the electrodes are mounted within conduit means.

30. A fuel cell or battery as claimed in claim 28 or claim 29 wherein the electrode that generates the mobile ionic species is located upstream of the electrode that consumes that mobile ionic species.

31. A fuel cell or battery as claimed in any one of claims 28 to 30 comprising a stack of electrodes connected in parallel.

32. A fuel cell or battery as claimed in claim 32 wherein the electrodes are separated a small gap or by a functionally inert porous membrane or by a porous electrolyte membrane.

33. A fuel cell or battery as claimed in any one claims 28 to 30 comprising a stack of electrodes connected in series.

34. A fuel cell or battery as claimed in claim 33 wherein an anode is separated from its immediate downstream neighbouring cathode by a small gap or by a functionally inert porous membrane or by a porous electrolyte membrane.

35. A fuel cell or battery as claimed in claim 2 or any one of claims 6 to 27 when dependent on claim 2 wherein the electrodes are disposed in an orientation substantially parallel to the direction of flow of the

mixture.

36. A fuel cell or battery as claimed in claim 35  
wherein the electrodes comprise a series connected array  
5 of multiple cells.

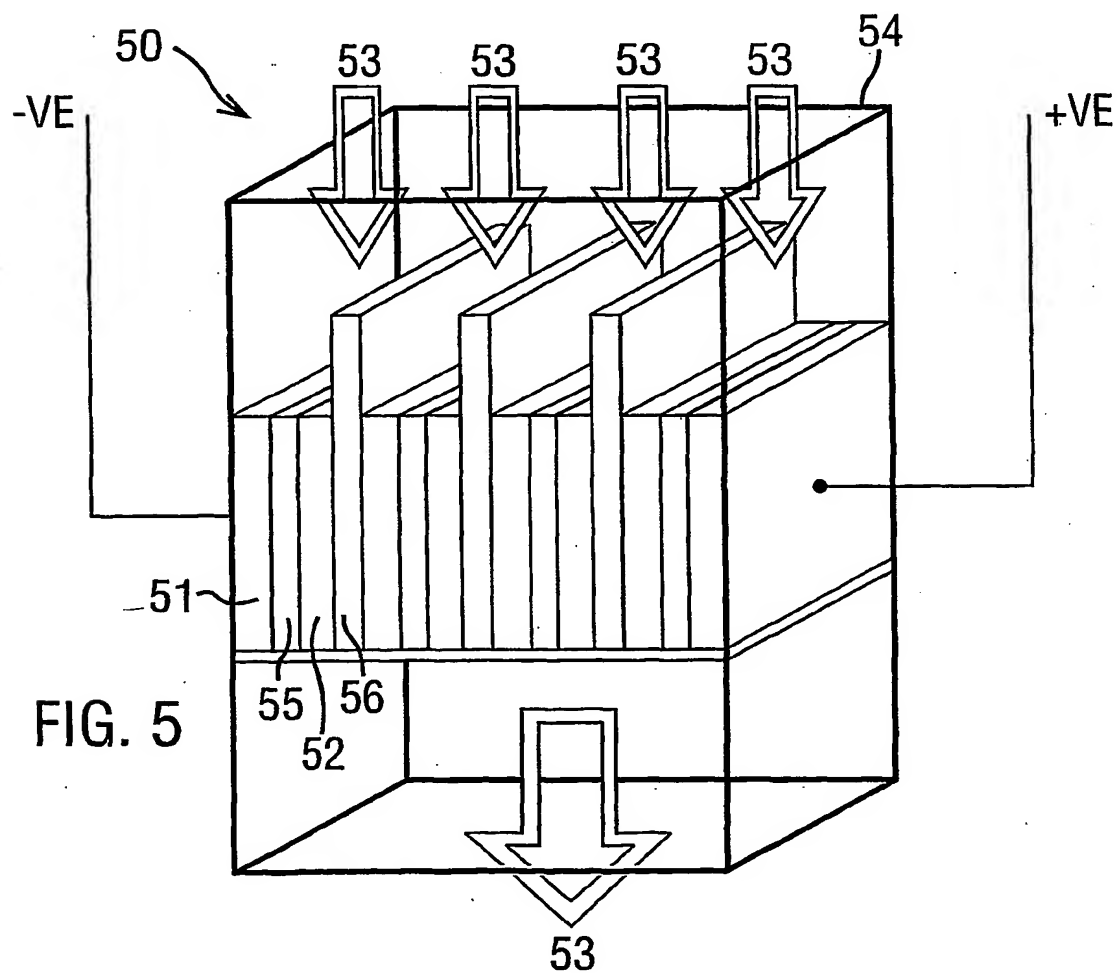
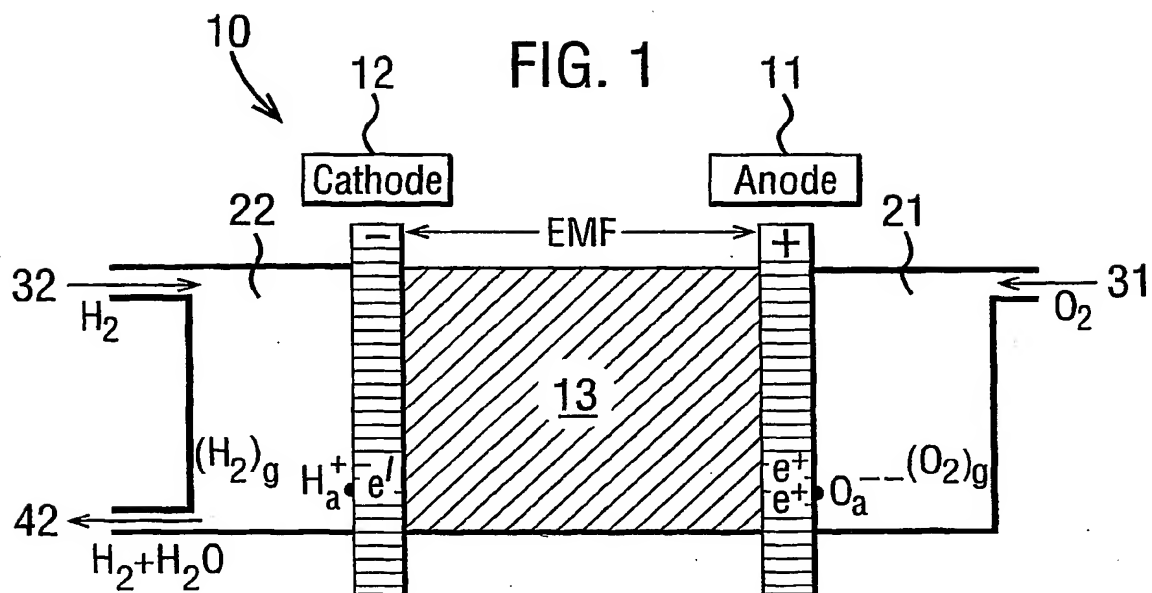
37. A fuel cell or battery as claimed in claim 35 or  
claim 36 wherein at least one further set of electrodes  
is provided downstream of a first set of electrodes.

10

38. A fuel cell or battery as claimed in claim 37  
wherein the at least one more set of electrodes is  
positioned downstream of said first set of electrodes  
with opposed polarities in corresponding portions of the  
15 flowpath such that the second anode or anodes are  
disposed downstream of the first cathode or cathodes and  
such that the second cathode or cathodes are disposed  
downstream of the first anode or anodes.

1/7

FIG. 1



2/7

FIG. 2

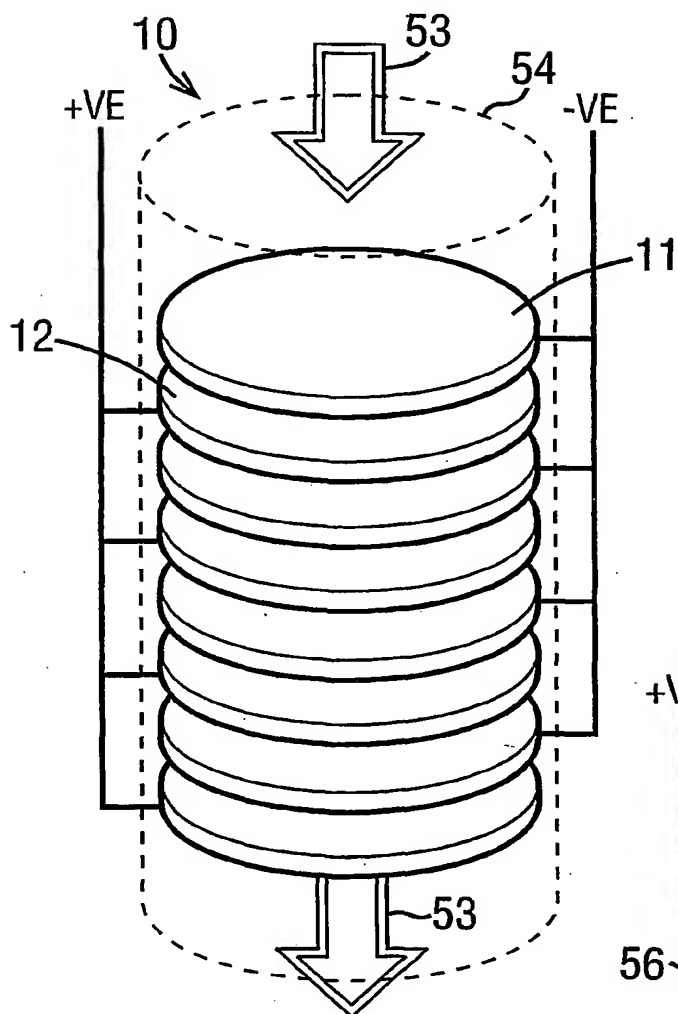
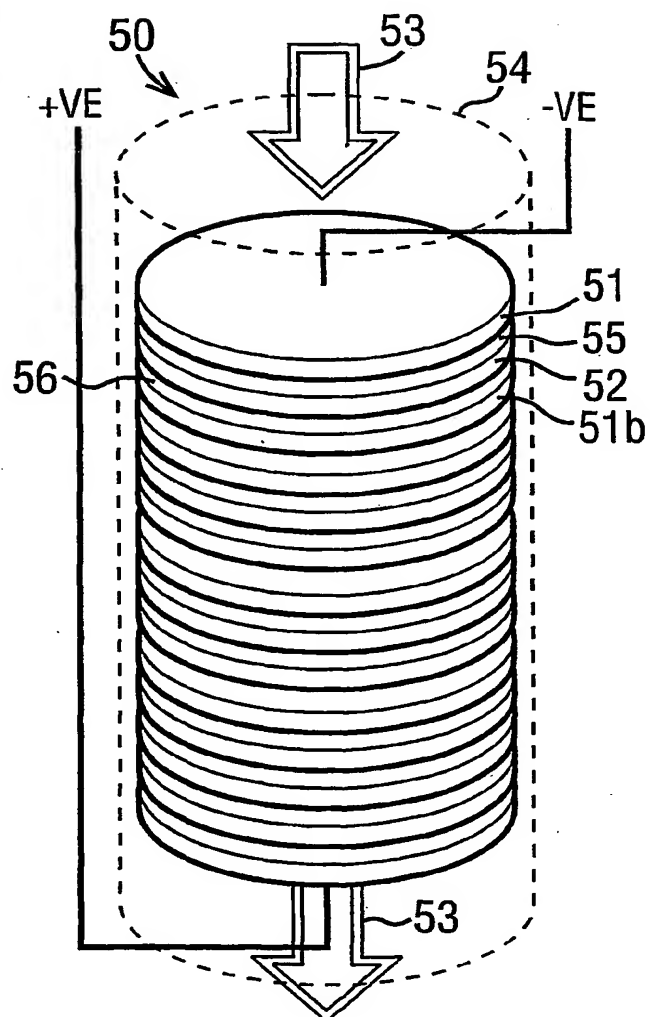
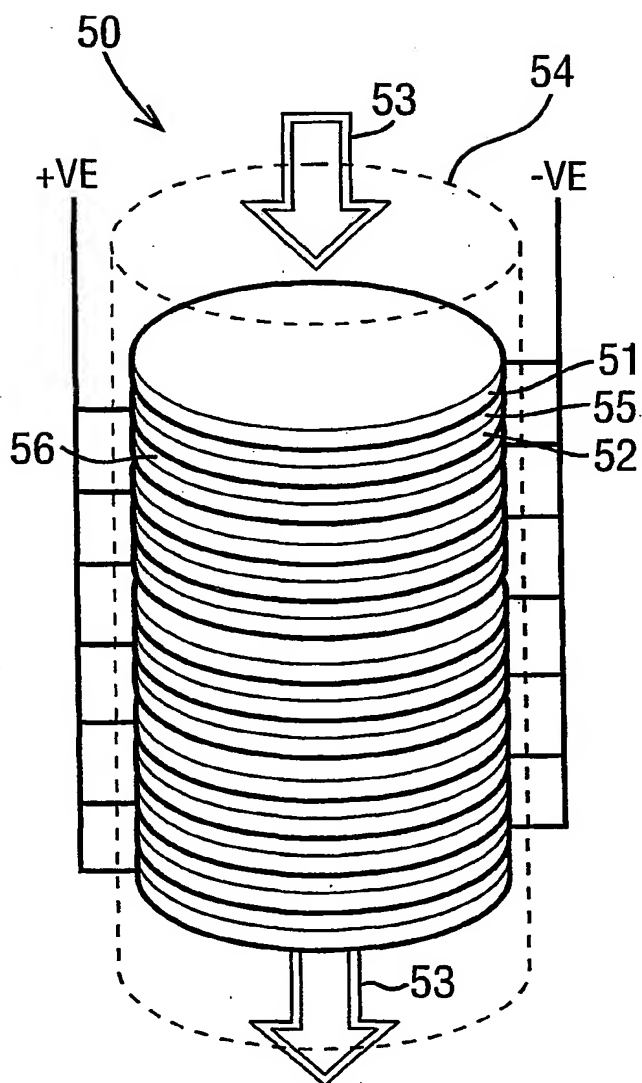


FIG. 3



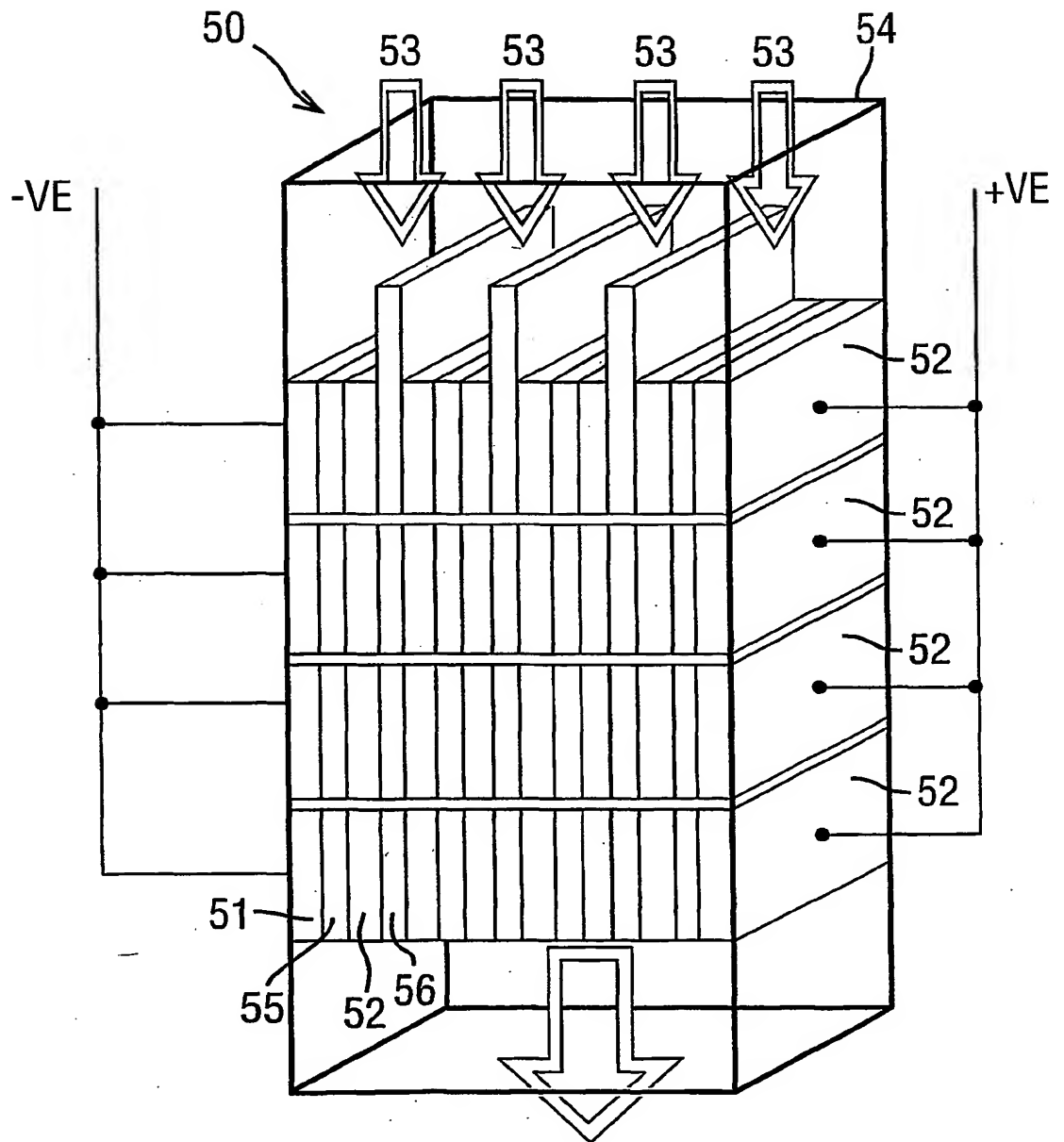
3/7

FIG. 4



4/7

FIG. 6



5/7

FIG. 7

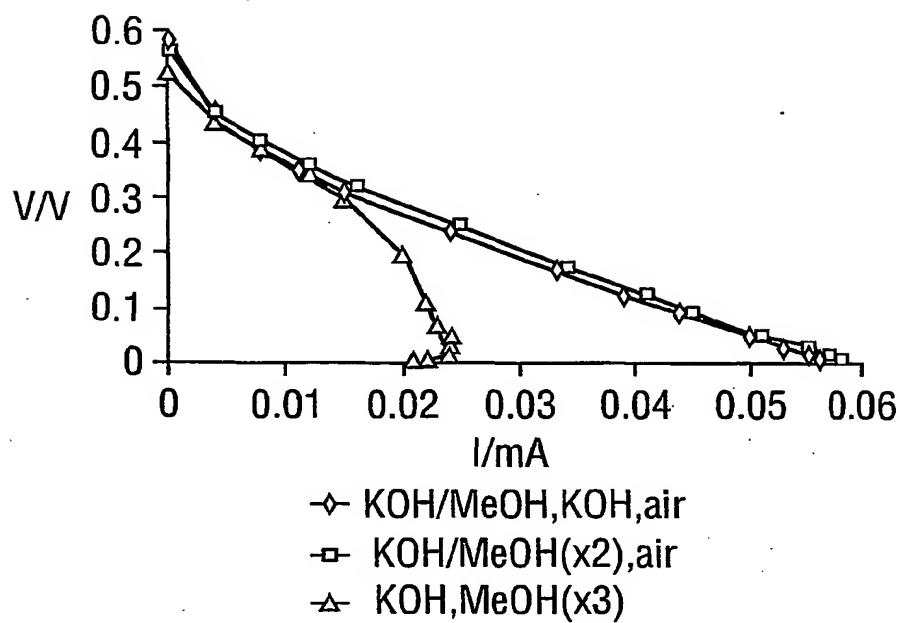
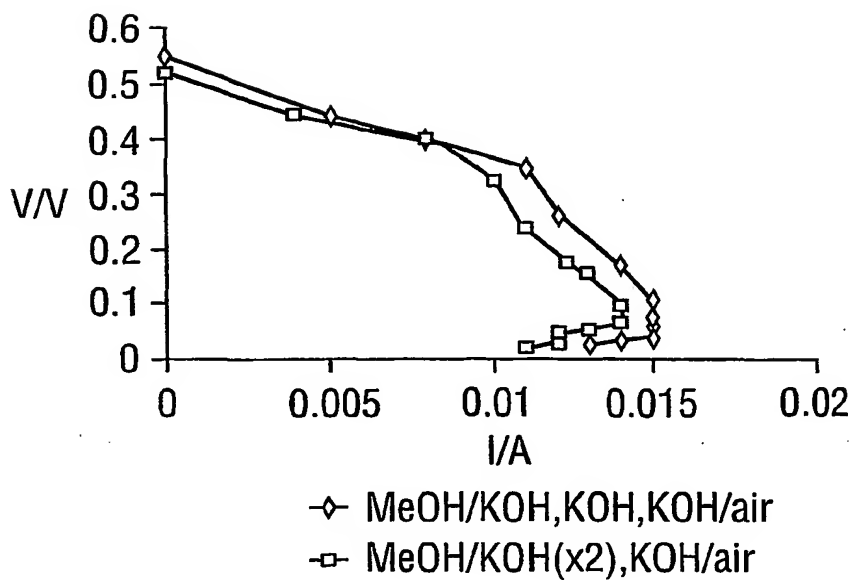


FIG. 8



6/7

FIG. 9

KOH/MeOHx3

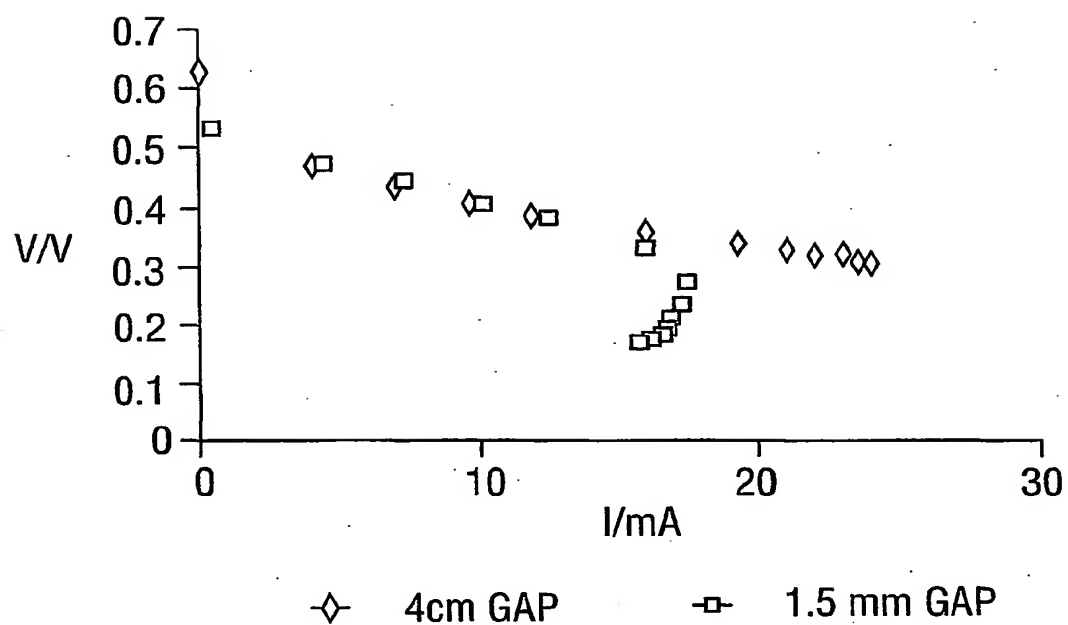
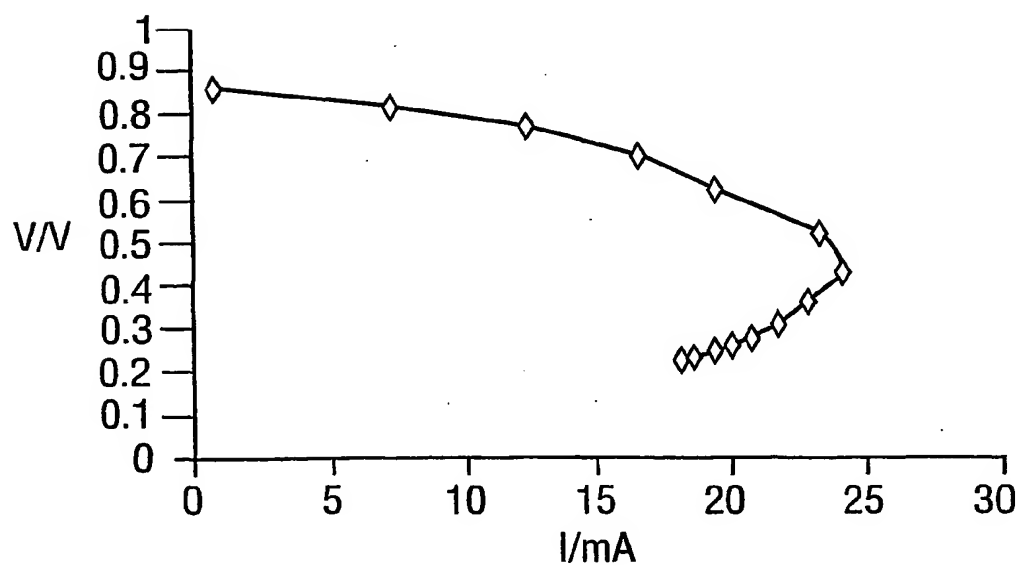


FIG. 10





7/7

FIG. 11

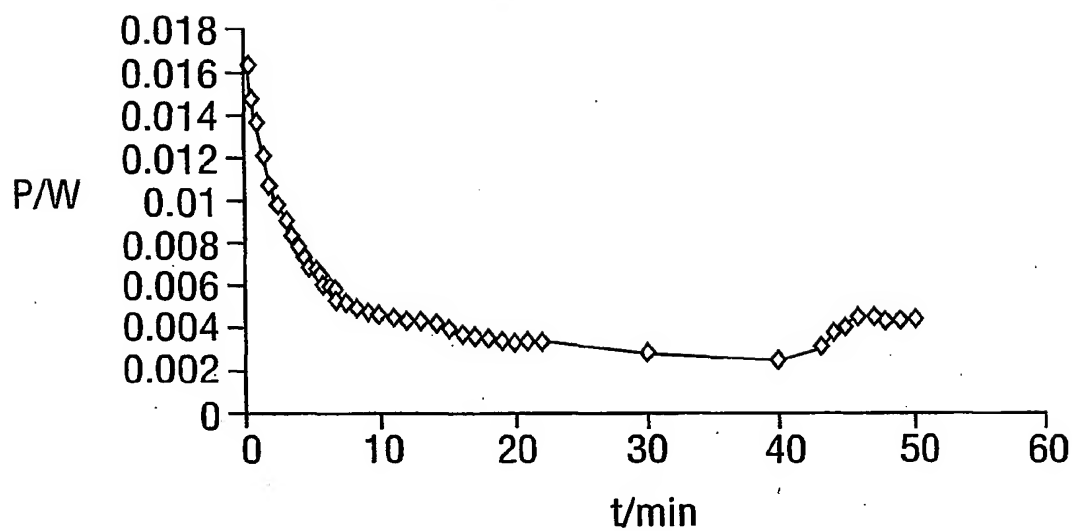
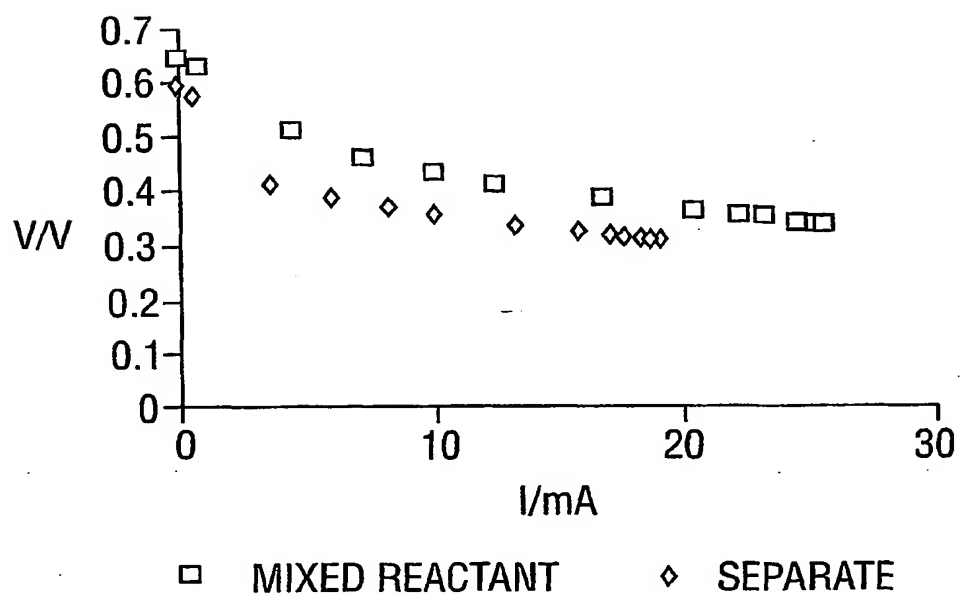


FIG. 12



## INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT/GB 01/01339

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/10 H01M8/08 H01M8/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 313 306 A (JOHNSON MATTHEY PLC) 26 April 1989 (1989-04-26) page 6, line 10 - line 20; claims 1-15 ---	1-38
A	US 3 719 529 A (LAKE D) 6 March 1973 (1973-03-06) claims 1-6 ---	1-38
A	US 4 248 941 A (LOUIS GEORGE A ET AL) 3 February 1981 (1981-02-03) claims 1-21 --- -/--	1-38



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

3 September 2001

Date of mailing of the international search report

10/09/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Battistig, M

# INTERNATIONAL SEARCH REPORT

Intern: Application No  
PCT/GB 01/01339

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>RIESS I ET AL: "Solid oxide fuel cells operating on uniform mixtures of fuel and air"</p> <p>SOLID STATE IONICS, NORTH HOLLAND PUB. COMPANY. AMSTERDAM, NL, vol. 82, no. 1, 15 November 1995 (1995-11-15), pages 1-4, XP004050226</p> <p>ISSN: 0167-2738</p> <p>cited in the application</p> <p>page 1 -page 4</p> <p>-----</p>	1-38

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: Application No

PCT/GB 01/01339

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0313306	A	26-04-1989	CA 1305515 A JP 1200566 A US 5004424 A	21-07-1992 11-08-1989 02-04-1991
US 3719529	A	06-03-1973	NONE	
US 4248941	A	03-02-1981	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)